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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

FA-0824

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR)

09/913574INTERNATIONAL APPLICATION NO.
PCT/US00/06960INTERNATIONAL FILING DATE
16 MARCH 2000 (16.03.00)PRIORITY DATE CLAIMED
17 MARCH 1999 (17.03.99)

TITLE OF INVENTION

HIGH SOLID EPOXY, MELAMINE AND ISOCYANATE COMPOSITIONSAPPLICANT(S) FOR DO/EO/US
NAGATA, Isao et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information

1. This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. This is an express request to being national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. A copy of the International Application was filed (35 U.S.C. 371 (c) (2))
 - a. is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. has been transmitted by the International Bureau.
 - c. is not required, as the application was filed in the United States Receiving Office (RO/US)
6. A translation of the International Application into English (35 U.S.C. 371 (c) (2)).
7. A copy of the International Search Report (PCT/ISA/210).
8. Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c) (3))
 - a. are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. have been transmitted by the International Bureau.
 - c. have not been made; however, the time limit for making such amendments has NOT expired.
 - d. have not been made and will not be made.
9. A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
10. An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. A copy of the International Preliminary Examination Report (PCT/IPEA/409)
12. A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 18 below concern document(s) or information included :

13. An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. A **FIRST** preliminary amendment.
A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. A substitute specification.
17. A change of power of attorney and/or address letter.
18. Certificate of Mailing by Express Mail.
19. Other items or information:

17. General Power of Attorney**18. Express Mailing Label No.: EJ376014762US**

APPLICATION NO. (IF KNOWN, SEE 37 CFR) 89/913574	INTERNATIONAL APPLICATION NO. PCT/US00/06960	ATTORNEY'S DOCKET NUMBER FA-0824																
20. The following fees are submitted		CALCULATIONS PTO USE ONLY																
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) – (5)) :																		
<input checked="" type="checkbox"/> Search Report has been prepared by the EPO or JPO \$860.00 <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) \$690.00 <input type="checkbox"/> No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$760.00 <input type="checkbox"/> Neither international preliminary examination fee paid to USPTO (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$1000.00 <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) And all claims satisfied provisions of PCT Article 33(2)-(4) \$ 100.00																		
ENTER APPROPRIATE BASIC FEE AMOUNT =		\$860.00																
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).		<input type="checkbox"/> 20 <input type="checkbox"/> 30 \$0.00																
<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 25%;">CLAIMS</th> <th style="width: 25%;">NUMBER FILED</th> <th style="width: 25%;">NUMBER EXTRA</th> <th style="width: 25%;">RATE</th> </tr> </thead> <tbody> <tr> <td>Total Claims</td> <td>56 - 20 =</td> <td>36 x</td> <td style="text-align: right;">\$18.00</td> </tr> <tr> <td>Independent Claims</td> <td>4 - 3 =</td> <td>36 x</td> <td style="text-align: right;">\$80.00</td> </tr> <tr> <td colspan="3">Multiple Dependent Claims (check if applicable)</td> <td style="text-align: right;"><input checked="" type="checkbox"/> \$270.00</td> </tr> </tbody> </table>		CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	Total Claims	56 - 20 =	36 x	\$18.00	Independent Claims	4 - 3 =	36 x	\$80.00	Multiple Dependent Claims (check if applicable)			<input checked="" type="checkbox"/> \$270.00	
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TOTAL OF ABOVE CALCULATIONS =		\$998.00																
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TOTAL NATIONAL FEE =		\$1,858.00																
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).		<input type="checkbox"/> \$0.00																
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<input type="checkbox"/> A check in the amount of _____ to cover the above fees enclosed. <input checked="" type="checkbox"/> Please charge my Deposit Account No. 04-1928 in the amount of \$1,858.00 to cover the above fees. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. 04-1928 a duplicate copy of this sheet is enclosed.																		
NOTE : Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (CFR 1.37(a) or (b)) must be filed and granted to restore the application to pending status.																		
SEND ALL CORRESPONDENCE TO: <div style="border: 1px solid black; padding: 10px; margin-bottom: 10px;"> DESHMUKH, Sudhir G. E. I. DU PONT DE NEMOURS AND COMPANY Legal Patent Records Center 1007 Market Street Wilmington, Delaware 19898 United States of America </div> <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> SIGNATURE  NAME DESHMUKH, SUDHIR G. REGISTRATION NUMBER 33,677 DATE 9 August 2001 </div> </div>																		

TITLE
HIGH SOLID EPOXY, MELAMINE
AND ISOCYANATE COMPOSITIONS

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BACKGROUND OF INVENTION

The present invention generally relates to high solids low VOC (volatile organic component) coating compositions and more particularly to low VOC clear coating compositions suited for multi-layered coatings used in automotive OEM and refinish applications.

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Basecoat-clearcoat systems have found wide acceptance in the past decade as automotive finishes. Continuing effort has been directed to such coating systems to improve the overall appearance, the clarity of the topcoat, and the resistance to deterioration. Further effort has been directed to the development of coating compositions having low volatile organic content (VOC). A continuing need exists for clear coating formulations which provide an outstanding balance of performance characteristics after application, particularly solvent and mar and etch-resistance.

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Examples of compositions used to form a protective coatings include those disclosed in U.S. Patent No. 4,533,716 (Okoshi et al.). These compositions are prepared using a triazine-type resin formed by a co-condensation reaction with formaldehyde, a polyol, and as required a monohydric alcohol. The polyols used in the condensation reaction may be prepared by an esterification reaction between higher fatty acids and epoxy compounds having a number average molecular weight of 174 to 4,000. The polyols used in the 4,533,716 invention do not include epoxy compounds. The 4,533,716 coating compositions are disclosed to include a triazine-type resin and a polyisocyanate.

20

The present invention is directed to a clear coating composition comprising isocyanate, melamine, and epoxy components wherein the isocyanate component comprises an aliphatic polyisocyanate having on an average 2 to 6 isocyanate functionalities.

25

The present invention is also directed to a method of producing a clear coating on a substrate comprising:
applying a layer of a clear coating composition comprising isocyanate, melamine, and epoxy components wherein the isocyanate component comprises an aliphatic

polyisocyanate having on an average 2 to 6 isocyanate functionalities, and curing the layer into the clear coating.

One of the advantages of the present invention is its low VOC, significantly below the current guidelines of Environment Protection Agency (EPA) of the United States.

Another advantage is etch and mar resistance of the coating resulting from the coating composition of the present invention.

Yet another advantage is the clarity of the coating resulting from the coating composition of the present invention.

10 As used herein:

“Two-pack coating composition” means a thermoset coating composition comprising two components stored in separate containers. These containers are typically sealed to increase the shelf life of the components of the coating composition. The components are mixed prior to use to form a pot mix. The pot mix has a limited potlife typically of minutes (5 minutes to 45 minutes) to a few hours (4 hours to 6 hours). The pot mix is applied as a layer of desired thickness on a substrate surface, such as an autobody. After application, the layer is cured under ambient conditions or cure-baked at elevated temperatures to form a coating on the substrate surface having desired coating properties, such as high gloss, mar-resistance and resistance to environmental etching.

“Low VOC coating composition” means a coating composition that includes less than 0.48 kilograms of organic solvent per liter (4 pounds per gallon) of the composition, as determined under the procedure provided in ASTM D3960.

25 “High solids composition” means a coating composition having solid component in the range of from 65 to 100 percent and preferably greater than 70 percent, all in weight percentages based on the total weight of the composition.

“Clear coating composition” means a clear coating composition that produces upon cure, a clear coating having DOI (distinctness of image) and 20° gloss of more than 70.

30 “Polymer solids” or “Composition solids” means a polymer or composition in its dry state.

“Aliphatic” as employed herein includes aliphatic and cycloaliphatic materials.

35 “Crosslinkable” means that the individual components of the adduct contain functionality which react within the composition of the invention to give a coating of good appearance, durability, hardness and mar resistance.

Applicants have unexpectedly discovered that contrary to conventional approaches used in typical thermoset coating compositions, i.e., those involving a film forming polymer and crosslinking component, a very viable route lies in a combination of what would traditionally be considered crosslinking agents for 5 producing a unique low VOC high solids clear coating composition which provides coatings with superior properties, such as mar and etch resistance.

The clear coating composition includes isocyanate, melamine, and epoxy components. The isocyanate component includes an aliphatic polyisocyanate having on an average 2 to 6, preferably 2.5 to 6 and more preferably 3 to 4 isocyanate 10 functionalities. The coating composition includes in the range of from 35 percent to 70 percent, preferably in the range of from 40 percent to 65 percent and more preferably in the range of from 45 percent to 60 percent of the aliphatic polyisocyanate, the percentages being in weight percentages based on the total weight of composition solids.

15 Examples of suitable aliphatic polyisocyanates include aliphatic or cycloaliphatic di-, tri- or tetra-isocyanates, which may or may not be ethylenically unsaturated, such as 1,2-propylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, 2,3-butylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate, 2,2,4-trimethyl hexamethylene diisocyanate, 20 dodecamethylene diisocyanate, 1,3-cyclopentane diisocyanate, 1,2-cyclohexane diisocyanate, 1,4-cyclohexane diisocyanate, isophorone diisocyanate, 4-methyl-1,3-diisocyanatocyclohexane, trans-vinylidene diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, 3,3'-dimethyl-dicyclohexylmethane4,4'-diisocyanate, meta-tetramethylxylylene diisocyanate, polyisocyanates having isocyanurate structural 25 units such as the isocyanurate of hexamethylene diisocyanate and isocyanurate of isophorone diisocyanate, the adduct of 2 moles of a diisocyanate, such as hexamethylene diisocyanate, uretidiones of hexamethylene diisocyanate, uretidiones of isophorone diisocyanate or isophorone diisocyanate, and one mole of a diol such as ethylene glycol, the adduct of 3 moles of hexamethylene diisocyanate and 1 mole of 30 water (available under the trademark Desmodur N of Bayer Corporation, Pittsburgh, Pennsylvania or Tolonate HDT-LV from Rhodia Co., Cranbury, NJ.). If desired, the isocyanate functionalities of the polymeric isocyanate may be capped with a monomeric alcohol, isopropanol or isobutanol to prevent premature crosslinking in a one-pack composition. Some suitable monomeric alcohols include methanol, ethanol, 35 propanol, butanol and hexanol.

Some other suitable blockers include lactams, oximes, malonic esters, alkylacetooacetates, triazoles, pyrazoles (e.g. dimethyl pyrazole), phenols and amines. Compositions of the present invention include one or more melamine. A melamine used in the present invention includes, in part, alkylated melamine-formaldehyde resin. The alkylated melamine formaldehyde resin maybe partially or fully alkylated. As examples of partially alkylated melamines, Cymel 1158 Cymel 324, Cymen 327 (from Cytec Ind., from West Paterson, NJ), Resimine BM 9539 (from Solutia, Inc., St. Louis, Mo.) can be mentioned. As examples of fully aklykated melamines, Cymel 350, and Cymel 301 (from Cytec Co., from Cytec. Ind., West Paterson, NJ) and 10 Resimine 764 (from Solutia Inc., St. Louis, Mo.) can be mentioned. A composition of the present invention may comprise from about 10 weight percent to about 40 weight percent of a melamine, preferably from about 15 weight percent to 35 weight percent of a melamine.

Compositions of the present invention include one or more oligomeric 15 epoxy compounds, preferably containing at least two epoxy functionalities. Suitable oligomeric epoxy compounds containing a hydroxy functionality or (OH) group used in the practice of the present invention include, among others, sorbitol polyglycidyl ether such as DCE 358 (form Dixie Chemical Co., Houston, TX), diglycerol polyglycidy ether such as Denacol EX 421 (from Nagase Cehmical Co., Hyogo, Japan), glycerol polyglycidyl ether such as Denacol Ex 313 and EX 314 (from Nagase Chemical Co., Hyogo, Japan), and triglycidyl tris(2-hydroxyethyl) isocyanurate such as Denacol EX 421 (from Nagase Chemical Co., Hyogo, Japan). Suitable oligomeric epoxy compounds which typically do not contain significant 20 hydroxy functionality used in the practice of the present invention include, among others, di- and polyglycidyl ethers of polycarboxylic acid and di- and polyglycidyl ester of acids such as Araldite CY 184 (from Ciba-Geigy, Brewster, N.Y.), cycloaliphatic epoxide such as ERL 4221 (from Union Carbide, Danbury, CT), and polyglycol diepoxide such as DER 736 (from Dow Chemical Co., Midland, MI). A composition of the present invention comprises from about 10 weight percent to 25 about 40 weight percent of an eopxy compound, preferably from about 15 weight percent to 35 weight percent of an epoxy compound.

The coating composition preferably includes one or more catalysts to enhance crosslinking of the components on curing.

A preferable catalyst is an organotin catalyst such as dibutyltin dilaurate, 35 dibutyltin diacetate, dibutyltin oxide, and dibutyltin bis(acetoacetate) in an amount of generally ranges from 0.001 percent to 1.0 percent, preferably from 0.01 percent to

0.5 percent and more preferably from 0.05 percent to 0.2 percent, the percentages being in weight percentages based on the total weight of composition solids.

In addition, the above coating composition can include other suitable catalysts, such as conventional acid catalysts, for example blocked or unblocked phosphoric acid and sulfonic acid in an amount ranging from 0.1 percent to 2 percent, preferably in the range of from 0.2 percent to 1.0 percent. As examples of such acid catalysts, phenyl acid phosphate, butyl acid phosphate, octyl acid phosphate, dodecylbenzenesulfonic acid, para-toluenesulfonic acid and dinonylnaphthalene sulfonic acid, which are optionally blocked with amines such as dimethyl oxazolidine and 2-amino-2-methyl-1-propanol can be mentioned.

The coating composition of the present invention, which is formulated into high solids coating systems may also contain at least one organic solvent typically selected from the group consisting of aromatic hydrocarbons, such as, petroleum naphtha or xylenes; ketones, such as, methyl amyl ketone, methyl isobutyl ketone, methyl ethyl ketone or acetone; esters, such as, butyl acetate or hexyl acetate; and glycol ether esters, such as propylene glycol monomethyl ether acetate. The amount of organic solvent added depends upon the desired solids level as well as the desired amount of VOC of the composition. If desired, the organic solvent may be added to both components of the binder. The amount of organic solvent used results in the composition having a VOC of less than 0.48 kilogram/liter (4 pounds per gallon), preferably in the range of 0.1 kilogram/liter to 0.4 kilogram/liter (1 pound to 3 pounds per gallon) of an organic solvent per liter of the composition.

The coating composition of the present invention may also contain conventional additives, such as, stabilizers, and rheology control agents, flow agents, and toughening agents. Such additional additives will, of course, depend on the intended use of the coating composition. Any additives that would adversely effect the clarity of the cured coating will not be included as the composition is used as a clear coating. The foregoing additives may be added to either component or both, depending upon the intended use of the coating composition.

To improve weatherability of the clear finish of the coating composition, about 0.1-5%, by weight, based on the weight of the composition solids, of an ultraviolet light stabilizer or a combination of ultraviolet light stabilizers may be added. These stabilizers include ultraviolet light absorbers, screeners, quenchers and specific hindered amine light stabilizers. Also, about 0.1-5% by weight, based on the weight of the composition solids, of an antioxidant can be added. Typical ultraviolet light stabilizers that are useful include benzophenones, such as

hydroxydodecylbenzo-phenone, 2,4-dihydroxybenzophenone; triazoles, such as 2-phenyl-4-(2'-4'-dihydroxybenzoyl)triazoles; and triazines, such as 3,5-dialkyl-4-hydroxyphenyl derivatives of triazine and triazoles such as 2-(benzotriazole-2-yl)-4,6-bis(methylethyl-1-phenyl ethyl)phenol, 2-(3-hydroxy-3,5'-di-tert amyl phenyl)benzotriazole, 2-(3',5'-bis(1,1-dimethylpropyl)-2'-hydroxyphenyl)-2H-benzotriazole, benzenepropanoic acid, 3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxy-C7-9-branched alkyl esters, and 2-(3',5'-bis(1-methyl-1-phenylethyl)-2'-hydroxyphenyl)benzotriazole.

Typical hindered amine light stabilizers are bis(2,2,6,6-tetramethylpiperidinyl)sebacate, bis(N-methyl-2,2,6,6-tetramethylpiperidinyl)sebacate and bis(N-octyloxy-2,2,6,6-tetramethylpiperidynyl)sebacate. Particularly useful blend of ultraviolet light absorbers and hindered amine light stabilizers is bis(N-octyloxy-2,2,6,6-tetramethylpiperidynyl)sebacate and benzenepropanoic acid, 3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxy-,C7-9-branched alkyl esters.

The coating composition of the present invention optionally contains, in the range of 0.5 weight percent to 15 weight percnt, preferably 1 weight percent to 10 weight percent of polyhydroxy functional compounds such as polycarbonate polyol (formula shown in the example), 2-ethyl-1,3-hexanediol, polycaprolactone triol, and the adduct of epsilon caprolactone and 1,3,5-tris(2-hydroxyethyl) cyanuric acid, all percentages being based on the total weight composition solids.

The coating composition of the present invention optionally contains in the range of from 0.5 percent to 30 percent, preferably in the range of from 1 percent to 20 percent, stabilized crosslinked polymer particles, non-aqueous dispersion (NAD) (as described in detail in U.S. Patent 4,960,828), all percentages being based on the total weight of composition solids.

The clear coating composition of the present invention may be supplied in the form of a two-pack coating composition in which a first pack includes the polyisocyanate and a second-pack includes the melamine, epoxy compounds and other additives.

Generally, the first and the second pack are stored in separate containers and mixed before use. The containers are preferably sealed air tight to prevent reactions during storage.

Alternatively, when the isocyanate funtionalities of the polyisocyanate are blocked, all components of the composition can be stored in the same containers in the form of a one-pack coating composition.

In use, the first-pack of the two-pack coating composition containing the polyisocyanate and the second-pack containing the melamine, epoxy compounds, and other additives are mixed just prior to use for about 1 to 15 minutes before use to form a pot mix, which has limited pot life, in range of from 5 minutes to 6 hours, 5 before it becomes too viscous to permit application through conventional application systems, such as spraying. Alternatively, the first pack and the second pack are mixed together at the plural spray gun with or without electrostatics, before applied to a substrate. Other methods of applications include roller coating, dipping or brushing and other conventional application methods. The layer of the coating composition 10 then cures under ambient conditions or preferably at higher temperatures in the range of 80-160°C for 10 minutes to 3 hours, preferably in the range of 20 minutes to 1 hour to form a coating on the substrate having the desired coating properties.

When the one-pack coating composition containing the blocked polyisocyanate is used, a layer thereof applied over a substrate using aforescribed 15 application techniques, is cured at a baking temperature in the range of from 80°C to 200°C, preferably in the range of 80°C to 160°C, for about 10 to 60 minutes. It is understood that actual baking temperature would vary depending upon the catalyst and the amount thereof, thickness of the layer being cured, the blocked isocyanate functionalities and the melamine utilized in the coating composition. The use of the 20 foregoing baking step is particularly useful under Original Equipment Manufacturer (OEM) condition.

It is understood that the actual curing time depends upon catalyst type and amount, the thickness of the applied layer and on the presence or absence of any suitable drying devices, such as, fans that assist in continuously flowing air over the 25 coated substrate to accelerate the cure rate. Generally, a clearcoat layer having a thickness in the range of from 25 micrometers to 75 micrometers applied over a metal substrate, such as automotive body which is often precoated with other coating layers such as electrocoat, primer and basecoat; cures in 20 to 60 minutes at about 80°C to 160°C.

Testing Procedures

The following test procedures were used for generating data reported in the examples below:

Test	Test Method
Dry film thickness	ASTM D1400
Appearance	ASTM D523, VISUAL
20° Gloss	ASTM D523
DOI	ASTM D5767
Tukon Hardness	ASTM D1474
Mar resistance	ASTM D5178
Percent solids	ASTM D2369

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EXAMPLE

The following non-limiting examples will further illustrate the invention. All parts, percentages, ratios, etc., in the examples are by weight unless otherwise indicated. The following abbreviations listed in Table 1 are used throughout. The examples below are carried out using standard techniques, which are well known and routine to those skilled in the art, except where otherwise described in detail. These examples are illustrative, but do not limit the invention.

15

DEFINITIONS

ARALDITE CY 184	Oligomeric, Epoxy Resin, 100% Solid (Ciba-Geigy, Brewster, NY)
CYMEL 1158	Polymeric Melamine, 80% Solid (Cytec Co., West Paterson, NJ)
TINUVIN 384	Ultraviolet Light Screener, 100% Solid (Ciba-Geigy, Tarrytown, NY)
TINUVIN 292	Hindered Amino Light Stabilizer (Ciba-Geigy, Tarrytown, NY)

BYK 301	Flow Additive (Byk Chemie USA, Wallingford, CT)
Dibutyltin Dilaurate	Catalyst (from Air Products, Allentown, PA)
Phenyl Acid Phosphate	Catalyst (from Albright & Wilson Co., Glen Allen, VA)
2-Ethylhexyl Acetate	Solvent (from Eastman Chemical Co., Kingsport, TN)
TOLONATE HDT-LV	Isocyanate Timer, 100% Solid (from Rhodia Inc., Cranbury, NJ)
CYMEL 350	Monomeric Melamine 100% Solid (Cytec Co. West Paterson, NJ)
ERL 4221	Oligomeric Epoxy resin, 100% solid (Union Carbide, Danbury, CT)
Dodecylbenzenesulfonic acid salt of amionethyl-proponol	Catalyst (Kings Industry, Norwalk, CT)
DER 736	Oligomeric Epoxy Resin, 100% solid (Dow Chemical Co. Midland, MI)

Synthesis Example 1 Synthesis of polycarbonate PL1015

A 5 liter round bottom flask was fitted with stirrer, condenser, heating mantle, thermometer, and Dean Stark trap. To the reactor were charged 402.5 gm 5 trimethylolpropane, 501.6 gm neopentylglycol, 567.2 gm 1,6-hexanediol, 1063.2 gm diethylcarbonate, and 0.2 gm dibutyltindilaurate (all available from Aldrich Chemicals, Milwaukee, WI). The mixture was slowly heated under agitation until ethanol began to distill off at approximately 120°C. Temperature was allowed to slowly increase to 140°C. Distillation continued at 140°C for a total of 16 hours until 10 829.3 gm ethanol were removed. The material was then cooled and 89.8 gm methylamyl ketone was added. The reaction yielded 1,707.2 grams of polycarbonate polyol at 94.2% weight percent solids.

Protective Coating Example 1

Part A was prepared by combining the following ingredients: 20 parts of ARALDITE CY 184; 25 parts of CYMEL 1158; 2.0 parts of TINUVIN 384; 1.5 parts of TINUVIN 292; 0.68 parts of a solution comprising 10 weight percent of

- 5 BYK 301 in propylene monoethylether acetate; 5.0 parts of a solution of 1 weight percent of dibutyltin dilaurate in butyl acetate; 0.67 parts of a solution of 75 weight percent of phenyl acid phosphate in butanol; 2.0 parts of PL1015, and 5.26 parts of 2-ethylhexyl acetate. This mixture was then combined with 54.7 parts of TOLONATE HDT-LV as a part B to form a clear composition.

10 Separately, a steel substrate, which had been precoated with electrocoat
and primer was coated with a conventional waterborne bascoat to a thickness of 15
micron and prebaked at 82°C for 10 minutes. Then, the above clear composition was
sprayed over the above prebaked waterborne basecoat and baked at 140°C for 30
minutes.

- 15 The substrate was cooled and Protective Coating 1 was tested. Characteristics of Protective Coating 1 are illustrated in Table 1 as compared to a characteristics of Control Protective Coating (conventional 2K isocyanate/acrylic polyol clear composition which had been prepared similarly).

TABLE 1
CHARACTERISTICS OF PROTECTIVE COATINGS

sample	Protective Coating 1	Control Coating [acrylic polyol/iso)
% Solid	85.6	53.0
VOC (lbs/gal)	1.29	3.9
#4 Ford spray viscosity (sec)	100	30
Gloss (20 deg.)	95	89
DOI	97	97
Tukon hardness(Knoop)	13.3	11.1
Cleveland humidity (96 hour @ 60 C)		
Tape adhesion	No failure	No failure
Blister	No	No
Boiling water resistance (3h)		
Tape adhesion	No failure	No failure
blister	No	No
Gravel @ -20 deg. C (Note 1)	7	6
Percent gloss retention after dry mar (note 2)	96	91
Min. temp.(C) without spot of synthetic acid rain soln.	65	60

Note1) Rating based on 1-10 with 10 best

Note 2) Gloss retention after 10 rubbing cycles using an abrasive material

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As shown in Table 1, Clearcoat Example 1 clearly showed good appearance at very low VOC and gave good physical properties.

Protective Coating Example 2

Protective Coating 2 was prepared as follows: Parts A was prepared by combining 22.0 parts of ARALDITE CY 184, 25.0 parts of CYMEL 1158, 2.0 parts of TINUVIN 384, 1.5 parts of TINUVIN 292, 0.68 parts of a solution of 10 weight percent of BYK 301 in propylene ethyl ether acetate, 5.0 parts of a solution of 1 weight percent dibutyltin dilaurate in butyl acetate, 0.67 parts of a solution of 75 weight percent of phenyl acid phosphate in butanol and 5.26 parts of 2-ethylhexyl acetate. The above part A mixture was then combined with 54.7 parts of TOLONATE HDT-LV as a part B to form a clear composition. The composition had a solid content of 85.6 weight percent, and a volatile organic compounds concentration of 1.29 lbs/gal. (0.15 Kg/liter).

The composition was then sprayed over a conventional silver metallic waterborne basecoat which had been applied to the similar substrate as described in Example 1 and prebaked at 82°C for 10 minutes, and baked at 140°C for 30 minutes similar to Example 1. The coating exhibited gloss 95, DOI 95 and Tukon hardness 11.3.

Protective Coating Example 3.

Protective Coating 3 was prepared as follows: Part A was prepared by mixing 20.0 parts of ARALDITE CY 184, 12.5 parts of CYMEL 1158, 10.0 parts of CYMEL 350, 2.0 parts of TINUVIN 384, 1.5 parts of TINUVIN 292, 0.68 parts of a solution of 10 weight percent of BYK 301 in propylene monoethyl ether acetate, 0.5 parts of a solution of 10 weight percent of dibutyltin dilaurate in Butyl acetate, 0.67 parts of a solution of 75 weight percent of phenyl acid phosphate in butanol, 2.0 parts of PL1015 and 10.26 parts of 2-ethylhexyl acetate. This part A mixture was then combined with 54.7 parts of TOLONATE HDT-LV as part B to form a clear composition. The clear composition had a solid content of 87.1 weight percent, and a volatile organic compounds concentration of 1.18 lbs/gal. (0.14 Kg/liter).

The composition was then sprayed over a conventional silver metallic waterborne basecoat which had been applied to the similar substrate as described in Example 1 and prebaked at 82°C for 10 minutes, and baked at 140°C for 30 minutes similar to Example 1. The coating exhibited gloss 94, DOI 94 and Tukon hardness 11.4.

Protective Coating Example 4

Protective Coating 4 was prepared as follows: Part A was prepared by mixing 20 parts of ERL 4221, 25 parts of CYMEL 1158, 2.0 parts of TINUVIN 384, 1.5 parts of TINUVIN 292, 0.68 parts of a solution of 10 weight percent of BYK 301 in propylene monoethyl ether acetate, 0.5 parts of a solution of 10 weight percent dibutyltin dilaurate in butyl acetate, 1.4 parts of dodecylbenzenesulfonic acid salt of amionethylpropanol, 2.0 parts of PL 1015, and 5.26 parts of 2-ethylhexyl acetate. This part A mixture was then combined with 54.7 parts of TOLONATE HDT-LV as a part B to form a clear composition. The clear composition had a solid content of 88.44 weight percent, and a volatile organic compounds concentration of 1.05 lbs/gal (0.12 Kg/liter].

The composition was then sprayed over a conventional silver metallic waterborne basecoat which had been applied to the similar substrate as described in Example 1 and prebaked at 82°C for 10 minutes, and baked at 140°C for 30 minutes similar to Example 1. The coating exhibited gloss 90, DOI 90 and Tukon hardness 4.6.

Protective Coating Example 5

Protective Coating 5 was prepared as follows: Part A was prepared by mixing 20.0 parts of DER 736 20.0 parts of CYMEL 350, 2.0 parts of TINUVIN 384, 1.5 parts of TINUVIN 292, 0.68 parts of a solution of 10 weight percent BYK 301 in propylene monoethyl ether acetate, 6.0 parts of the salt of dodecylbenzenesulfonic acid and diethanolamine, 4.2 parts of PL1015 and 6.75 parts of 2-Ethylhexyl Acetate. This part A mixture was then combined with 52.5 parts of TOLONATE HDT-LV as a part B to form a clear composition. The composition had solid content of 88.0 weight percent, and a volatile organic compounds concentration of 1.09 lbs/gal.(0.13 Kilograms/liter).

The composition was then sprayed over a conventional silver metallic waterborne basecoat which had been applied to the similar substrate as described in Example 1 and prebaked at 82°C for 10 minutes, and baked at 140°C for 30 minutes similar to Example 1. The coating exhibited gloss 87, DOI 90 and Tukon hardness 3.6.

The complete disclosures of all patents, patent applications, and publications are incorporated herein by reference as if individually incorporated. Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and

should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

WHAT WE CLAIM IS:

1. A low VOC clear coating composition comprising isocyanate, epoxy compound and melamine components wherein said isocyanate component comprises an aliphatic polyisocyanate having an average of 2 to 6 isocyanate functionalities.
2. The composition of claim 1 wherein said composition further comprises a catalyst.
- 10 3. The composition of claim 2 wherein said catalyst is selected from the group consisting of an organotin catalyst, acid catalyst and combinations thereof.
4. The composition of claim 3 wherein said organotin catalyst is selected from the group consisting of dibutyltin diacetate, dibutyltin dilaurate, dibutyltin oxide, dibutyltin bis(acetoacetate) and combinations thereof.
- 15 5. The composition of claim 3, wherein said acid catalyst is selected from the group consisting of phenyl acid phosphate, butyl acid phosphate, octyl acid phosphate, dodecylbenzenesulfonic acid, para-toluenesulfonic acid, dinonylnaphthalenesulfonic acid and combinations thereof.
- 20 6. The composition of claim 3 or 5, wherein said acid catalyst is blocked with an amine.
- 25 7. The composition of claim 6, wherein said amine is dimethyloxazolidine, 2-amino-2-methyl-1-propanol, di(2-hydroxyethyl)amine or a combination thereof.
8. The composition of claim 2,3,4,5 or 6 wherein said composition comprises about 0.001 weight percent to about 3.0 weight percent of catalyst, all percentages based on the total weight of composition solid.
- 30 9. The composition of claim 1 further comprises a polyhydroxyl functional compound.
- 35 10. The composition of claim 9 wherein said polyhydroxyl functional compound is a polycarbonate polyol.

11. The composition of claim 9 or 10 wherein said polyhydroxyl functional compound comprises from about 0.5 weight percent to about 15 weight percent of the composition.

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12. The composition of claim 1 further comprises a non-aqueous dispersion resin, stabilized dispersed polymer particles.

13. The composition of claim 1, wherein said epoxy compound is selected
10 from the group consisting of a polyglycidyl ester of an acid, a polyfunctional aliphatic epoxy compound, a cycloaliphatic epoxy compound, a polyfunctional cycloaliphatic epoxy compound or combinations thereof.

14. The composition of claim 1 or 13, wherein said epoxy compound is a di
15 or polyglycidyl ester of a di or polycarboxylic acid.

15. The composition of claim 1, 13 or 14, wherein said epoxy compound comprises from about 10 weight percent to about 40 weight percent of the composition.

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16. The composition of claim 1, wherein said melamine is a fully alkylated melamine-formaldehyde resin.

17. The composition of claim 1, wherein said melamine is a partially
25 alkylated melamine-formaldehyde resin.

18. The composition of claim 1, 16 or 17, wherein said melamine compound comprises from about 10 weight percent to about 40 weight percent of the composition.

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19. The composition of claim 1 further comprises ultraviolet light absorbers, light stabilizers or a combination thereof.

20. The composition of claim 1, wherein said aliphatic polyisocyanate is
35 selected from the group consisting of trimers of hexamethylene diisocyanate,

isophorone diisocyanate, or meta-tetramethylene diisocyanate and combinations thereof.

21. The composition of claim 1 or 20, wherein said aliphatic polyisocyanate
5 is blocked.
22. The composition of claim 1, 20 or 21, wherein aliphatic polyisocyanate is
blocked by reacting with an aliphatic mono-alcohol.
- 10 23. The composition of claim 1, 20, 21 or 22, wherein said aliphatic
polyisocyanate comprises from about 35 weight percent to about 70 weight percent of
the composition.
- 15 24. The composition of claim 1 further comprises a solvent.
25. The composition of claim 1, wherein said composition has a solids
content of greater than 65 weight percent.
- 20 26. A composition of claim 1, wherein said composition has a solids content
of greater than 80 weight percent.
- 25 27. An article comprising a substrate having a first and a second major
surface and a layer of protective coating, the protective coating comprising a
hardened composition of claim 1.
28. The article of claim 27, wherein said substrate is selected from the group
consisting of metal, plastic, wood and rubber.
- 30 29. The article of claim 27, wherein said layer of protective coating has a
thickness of about 25 micrometers to about 75 micrometers.
- 30 30. The article of claim 27, wherein said layer of protective coating is acid-
resistant.
- 35 31. The article of claim 27, wherein said layer of protective coating is
transparent.

32. The article of claim 27, comprising a layer of electrocoat, primer and a layer of basecoat interposed between the substrate and the layer of protective coating.
- 5 33. A process of making a composition that upon hardening forms a protective coating comprising the steps of:
- combining an aliphatic polyisocyanate having an average of 2 to 6 isocyanate functionalities an epoxy compound, and melamine.
- 10 34. A process of making a composition that upon hardening forms a protective coating comprising the steps of :
- making a first mixture comprising an epoxy, a melamine;
- making a second mixture comprising an aliphatic polyisocyanate
- 15 35. having an average of 2 to 6 isocyanate functionalities; and
- combining the first and second mixtures
- wherein said first mixture, second mixture or both mixtures comprise a solvent.
- 20 36. The process of claim 34 wherein said first mixture, second mixture or both mixtures contain a solvent.
37. The product produced by the process of claim 34.
- 25 38. A process of making an article comprising the steps of:
- applying a composition comprising an aliphatic polyisocyanate having an average of 2 to 6 isocyanate functionalities, an epoxy compound, and melamine to a substrate; and hardening the composition.
- 30 39. The process of claim 37 wherein said composition is applied by spraying.

DECLARATION and POWER OF ATTORNEY

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

HIGH SOLID EPOXY, MELAMINE AND ISOCYANATE COMPOSITIONS

the specification of which is attached hereto unless the following box is checked:

was filed on 16 MARCH 2000 as U.S. Application No. _____ or PCT International Application No. PCT/US00/06960 and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is known to me to be material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Application No.	Country	Filing Date	Priority Claimed (Yes/No)
I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States Provisional Application(s) listed below.			
	U.S. Provisional Application No.		U.S. Filing Date
	60/124,850	17 MARCH 1999	
	60/131,146	24 APRIL 1999	
	60/131,145	27 APRIL 1999	

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International Application designating the United States, listed below, and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application or PCT International Application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is known to me to be material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application No.	Filing Date	Status (patented, pending or abandoned)
POWER OF ATTORNEY: I hereby appoint the following attorney(s) and/or agent(s) the power to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:		
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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Additional Inventors are being named on separately numbered sheets attached hereto.

GENERAL POWER OF ATTORNEY
(Concerning Several International Patent Applications)

The undersigned, Vernon R. Rice, Vice President and Assistant General Counsel of E. I. DU PONT DE NEMOURS AND COMPANY, 1007 Market Street, Wilmington, Delaware 19898 USA ("DuPont"), hereby confirms that the power to sign for DuPont has been granted to various individuals (as set forth in the attached excerpt from DuPont's Patent Board Rules of Procedure (January 1988), Appendix Section III.A.4), including the Chairman, Vice-Chairman, and those individuals who are Assistant Secretaries of the Patent Board. Currently these Assistant Secretaries are:

Roger A. Bowman
Linda J. Davis
John E. Griffiths

Barbara J. Massie
Miriam D. Meconnahey
Deborah A. Meginniss

In addition, the authority to act on behalf of DuPont before the competent International Authorities in connection with any and all international patent applications filed by it with the United States as Receiving Office and to make or receive payments on its behalf is hereby granted to:

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Evans, Craig H.	31,825	Santopietro, Lois A.	36,264
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Feltham, S. Neil	36,506	Sebree, Chyrea J.	45,348
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Frank, George A.	27,636	Shay, Lucas K.	34,724
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Gorman, Thomas W.	31,959	Siegell, Barbara C.	30,684
Gould, David J.	25,338	Sinnott, Jessica M.	34,015
Griffiths, John E.	32,647	Steinberg, Michael A.	43,160
Hamby, Jane O.	32,872	Steinberg, Thomas W.	37,013
Hamby, William H.	31,521	Stevenson, Robert B.	26,039
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Hendrickson, John S.	30,847	Tessari, Joseph A.	32,177
Joung, J. Kenneth	41,881	Tulloch, Rebecca W.	36,297
Katz, Elliott A.	26,396	Walker, P. Michael	32,602
Kelly, Patricia L.	39,247	Wang, Chen	38,650
King, Karen K.	34,850		

The undersigned ratifies fully all actions already taken by the above-named individuals in accordance with the authority granted hereby.

E. I. DU PONT DE NEMOURS AND COMPANY

By:

Vernon R. Rice

Vice President and Assistant General Counsel

Date: 9-13-00